Cluster Compounds of Gold

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In this paper the author reviews the work carried out under his direction in the laboratory of the Italian Research Council on the structure of an unusual class of compounds in which metal atoms in zero or low oxidation states are bonded to one another. The resolution of the configuration of the atoms in these interesting compounds may well improve our understanding of the electronic structure of metals and alloys.

The characteristic feature of the so-called metal cluster compounds is the presence of at least three metal atoms bound together in a non-linear configuration. Metal-metal bonds are judged to be present when the distances between pairs of metal atoms are of the same order of magnitude as in the metals: the bond lengths are sometimes taken as an indication of the relative strength of the bond and of the bond order.

Four main classes of metal cluster compounds are known at present:

(i) The alkali salts of polyanions of tin, lead, antimony and bismuth such as Na_4Sn_9, Na_4Pb_7, Na_3Sb_7, Na_3Bi_5 and Na_3Bi_3.

(ii) The lower halides of some transition metals, particularly those belonging to subgroups V A and VI A, and of bismuth.

(iii) The polynuclear metal carbonyls and their derivatives.

(iv) The polynuclear gold compounds with tertiary phosphines.

The cluster compounds of class (i) can be obtained only in anhydrous ammonia solution, and very little is known about their structure. Their anions are the only discrete clusters formed by bare metal atoms, without any other ligand. The presence of intermetallic bonds, even in the absence of direct proof, is clearly a necessary condition for their existence.

The compounds of class (ii) were the first to have their structures investigated. The molybdenum and tungsten derivatives, originally formulated as dihalides, e.g. "$MoCl_2$", were recognised by X-ray diffraction to be composed of groups of metal atoms in octahedral configurations, with intermetallic distances somewhat shorter than in the metals. The structure of the compound $Mo_6Cl_{12}(py)_2$, prepared by dissolution of "$MoCl_2$" in pyridine (py), is shown in Figure 1. Analogous structures have been found for the niobium and tantalum halides of empirical formula Nb_3X_7 and Ta_3X_7 (X=Cl, Br) respectively, which give rise in aqueous solution to octahedral cluster cations such as $[Ta_6Cl_{12}]^{2+}$, and for platinum dichloride, which has a polymeric structure based on Pt_6 octahedral clusters.

The class exhibiting the greatest number and variety of metal cluster compounds is class (iii), the polynuclear metal carbonyls and their derivatives. The types $M_4(CO)_{12}$ and $M_6(CO)_{16}$ (M=Co, Rh, Ir) are tetrahedral and octahedral respectively, but many other less regular structures have been found when the number of cluster atoms is odd and sometimes even when an octahedral arrangement would have been expected, as in the case of the carbonylhexaplatinate anion shown in Figure 2.

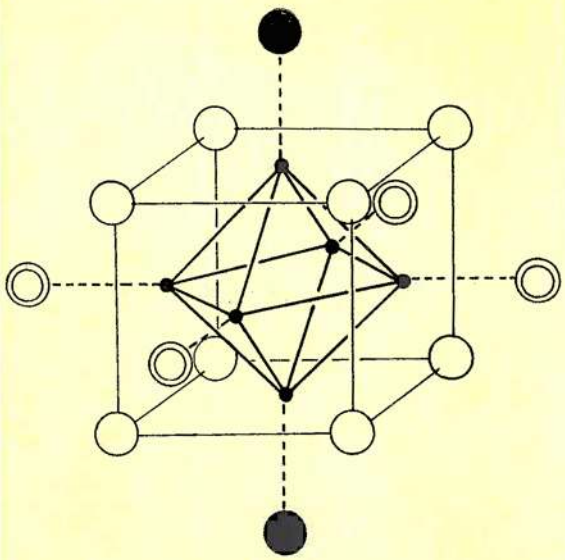

Fig. 1 The structure of $Mo_6Cl_{12}(py)_2$. The 6 Mo atoms form the internal octahedron. At the vertices of the cube there are 8 non-exchangeable Cl atoms (indicated as ○); 4 exchangeable Cl atoms (indicated as ◎) and 2 pyridine molecules (indicated as ●) are bonded at the vertices of the octahedron

The cluster gold compounds belonging to class (iv) were first obtained by the author and Naldini when trying to prepare the derivatives of gold(O) with tertiary phosphines. We presumed that, since the intermetallic bond in the Au_2 molecule (which is present in the gas phase) is rather strong and since the triarylphosphine (L) gold compounds LAuX are very stable, gold(O) derivatives of the type L·Au·Au·L should readily be obtained by reduction of LAuX with appropriate reagents.

However, by the action on these compounds of a variety of reducing agents such as sodium borohydride in ethanol, potassium hydroxide in methanol, and lithium aluminium hydride in tetrahydrofuran, only a partial reduction took place, with the formation of polynuclear gold derivatives whose formulae depended on the nature of the anion X and the phosphine L and, to a minor extent, on the preparative technique.

The gold cluster compounds, which are red, green or yellow, are stable in air, both in the solid state and in solution in organic solvents. Some are non-ionic, while in others the cluster is the cation of a salt-like compound. Those for which the structures have been determined by X-ray crystallography, have 6, 9 or 11 gold atoms in the cluster.

Gold Cluster Compounds of Known Structure

These may be assigned to three different types:

(*a*) $[Au_{11}L_7X_3]$, red, non-ionic;

(*b*) $[Au_9L_8]X_3$, green, ionic;

(*c*) $[Au_6L_6]X_2$, yellow, ionic.

Compounds of Type (a)

These are obtained by reduction of LAuX where X=I, CN, CNS. Seven have been prepared so far (1); they include four having X=CNS and L=$P(C_6H_5)_3$, $P(p\text{-}C_6H_4CH_3)_3$, $P(p\text{-}C_6H_4Cl)_3$, and $P(p\text{-}C_6H_4F)_3$ respectively and one having X=CN and L=$P(p\text{-}C_6H_4Cl)_3$. The crystallographic X-ray analysis showed that the same pattern is present in all these compounds: the preliminary structure has been resolved for $Au_{11}[P(C_6H_5)_3]_7(CNS)_3$ (2) and the complete structure has been determined for Au_{11} $[P(p\text{-}C_6H_4F)_3]_7I_3$ (3).

In this structure a central gold atom is surrounded, at an average distance of 2.68 Å, by 10 gold atoms at bonding distances from each other (2.98 Å) and each bound to an L or an X ligand. The coordination polyhedron formed by the gold atoms can be considered as a pentagonal bipyramid sharing a vertex with a square pyramid (Figure 3a), or it can be derived from a centred icosahedron in which, in the place of three atoms at the vertices of a triangular

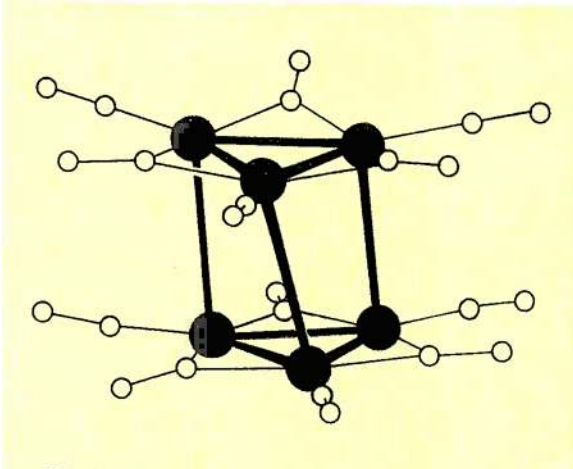

Fig. 2 A perspective view of the dodecacarbonylhexaplatinate cluster anion $[Pt_6(CO)_{12}]^{2-}$

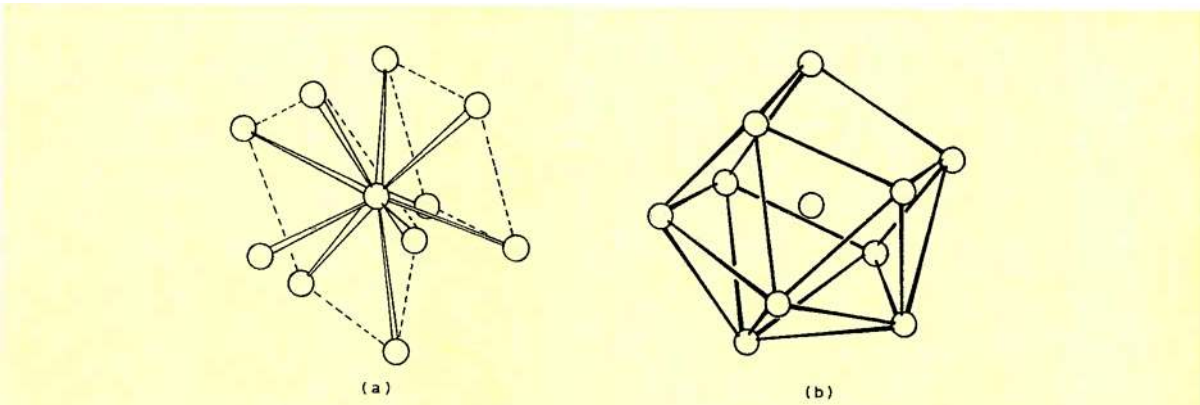

Fig. 3 Different interpretations of the structure of the Au_{11} cluster:
(a) Pentagonal bipyramid sharing a vertex with a tetragonal pyramid
(b) Modified centred icosahedron

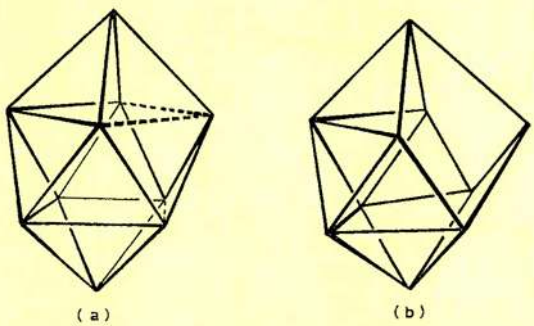

Fig. 4 Transformation of a dicapped antiprism (a) into an incomplete icosahedron (b) by stretching 3 edges

face, there is one atom at the centre of the missing face (Figure 3b).

In the first case the central atom has been considered as Au^0 (electronic configuration $5d^{10}\ 6s^1$), accepting 7 electrons from the AuL radicals bound to it, thus achieving the electronic configuration of radon ($5d^{10}6s^26p^6$). In the second case (icosahedral structure) the central atom has been considered Au^{III}, accepting 10 electrons, 7 from AuL radicals and 3 from $[AuX^-]$ radicals, again achieving the radon configuration. Furthermore the smaller Au^{III} atom could fit the cavity of the ideal icosahedron, which is only 0.9 times that of the 12 peripheral contact spheres.

However, when it became apparent that the noble gas electronic configuration is not achieved by the central gold atoms in compounds of class (b), a different explanation was proposed.

If one computes the number of electrons available for the gold atoms of the Au_{10} cage, one finds that there are 65, besides the complete 5*d* shells, which is just the number needed to fill 8 of the 9 orbitals of the peripheral atoms and leave 5 electrons for the central Au^0 atom, which thus also fills 8 of its 9 orbitals. This is not surprising since the I B subgroup metals (Cu, Ag, Au) often do not achieve the noble gas configuration in their compounds. The filling of 8 of the 9 gold valence orbitals may thus be taken, at least for the moment, as the key for understanding these compounds from an electronic point of view.

A *closo* Au_{10} cage should have the same pattern as a dicapped Archimedean antiprism, and in fact the incomplete icosahedron can be derived from the dicapped antiprism, as shown in Figure 4, by stretching three edges in order to make the central cavity large enough to lodge the Au^0 atom.

Compounds of Type (b)

These are prepared by an analogous method to that used for the class (a) compounds, but starting with LAuY, in which the anion Y has very poor coordinating properties, if any. Seven compounds of this class have so far been obtained (4) including the nitrate and the hexafluorophosphate of the cluster cation with $L{=}P(p\text{-}C_6H_4CH_3)_3$, as well as the perchlorate, the tetrafluoroborate, the hexafluorophosphate, and the picrate of the cluster cation with $L{=}P(C_6H_5)_3$.

A structural analysis has been carried out only on the hexafluorophosphate of the tri(*p*-tolyl)phosphine derivative: $[Au_9[P(p\text{-}C_6H_4CH_3)_3]_8][PF_6]_3$ (5), but preliminary X-ray structural analysis has shown that the same metal cluster is present in all the compounds.

In these structures the central gold atom is bound to 8 peripheral gold atoms, each attached to a phosphine ligand. The centre-to-periphery distances fall within two ranges: 2.689(3) and 2.729(3) Å and similarly the gold-gold distances in the periphery are 2.752(3) and 2.868(3) Å. All these distances are shorter than that found in the metal (2.884 Å). The geometry of the cluster may be considered as that of a centred icosahedron from which an equatorial rectangle has been removed (Figure 5a); in the ideal

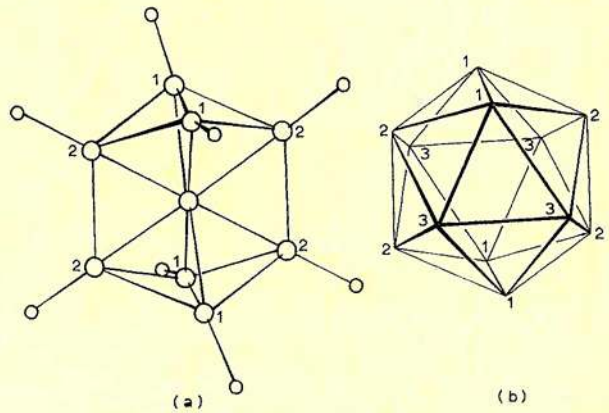

Fig. 5 (a) Structure of the Au_9 cluster in $[Au_9L_8]$ compounds. (b) The ideal icosahedron from which the positions of the 8 peripheral gold atoms can be derived by removing the rectangle labelled 3

icosahedron (Figure 5b), the rectangle to be removed is defined by the points labelled 3. An electron computation based on this structure indicates that all the gold atoms achieve a configuration with sixteen electrons, two electrons shorter than required by the rare gas rule, exactly as in the case of the compounds of type (a).

Compounds of Type (c)

Only one such compound has so far been prepared (6); it was obtained from the mother liquor from the preparation of a compound of class (b). This shows that the same starting materials can give rise to different compounds, but the influence of the conditions of the reaction on the products is still completely unknown.

The cluster is a hexameric cation of the very simple formula $[(AuL)_6]^{2+}$, the structure of which has been resolved for the bis(tetraphenylborate) salt. The cation has the shape of a weakly distorted centrosymmetric octahedron, squeezed along a C_3 axis (Figure 6).

If one makes a computation of the valence electrons for this structure, and makes a comparison with the octahedral $Rh_6(CO)_{16}$ cluster, which has two electrons in excess of the noble gas structure, one finds that, to fill 8 of the 9 orbitals of the gold atoms with two electrons in excess, the cluster should be $[Au_6L_6]^{4+}$. It is therefore assumed that the high charge density renders this hypothetical species unstable, so that another M.O., and possibly an antibonding one, is occupied, giving $[Au_6L_6]^{2+}$. This hypothesis offers an explanation of the fact that the Au-Au distances in the Au_6 cluster are somewhat longer than the peripheral distances in the Au_9 and Au_{11} clusters. But for this antibonding contribution, it would be expected that, in the centred Au_9 and Au_{11} clusters, the Au-Au distances should be longer, since the central atom is larger than the ideal cavity. The $[Au_6L_6]^{2+}$ cluster has some resemblance to $Cu_6L_6H_6$ (7), which is the only copper cluster compound of this class so far known and which also has an octahedral structure.

Compounds of Unresolved Structure

Many other gold cluster compounds for which no structural information is available have also been prepared (8). For these compounds molecular formulae assigned on the basis of elemental analysis should be treated with some reservation. For instance, the compound originally reported as $Au_5L_4Cl.4H_2O$ [$L=P(C_6H_5)_3$] was later reformulated as $[Au_{11}L_9Cl]Cl_2$ (9). A comparison of the analytical compositions corresponding to the two formulations shows that they are practically indistinguishable on the basis of chemical analysis [$Au_5L_4Cl.4H_2O$ requires C=40.3 per cent, H=3.25 per cent, Au=45.8 per cent, Cl=1.66 per cent and $[Au_{11}L_9Cl]Cl_2$ requires C=40.7 per cent, H=3.2 per cent, Au=45.5 per cent, Cl=2.4 per cent]. The analysis for chlorine, which should allow a distinction between the two formulations to be made, is of little help, since these compounds adsorb extraneous halide ions very tenaciously. However, the double exchange of $[Au_{11}L_9Cl]Cl_2$ with NaY salts [$Y=ClO_4^-$, PF_6^-, NO_3^-, $[B(C_6H_5)_4]^-$], giving $[Au_{11}L_9Cl]Y_2$ and the molar conductivities of these compounds, supports the new formulation. The cationic cluster $[Au_{11}L_9Cl]^{2+}$ would then represent a fourth type of gold cluster compound, which can be considered as being derived from the neutral cluster of type (a) by substitution of two coordinated anions by two neutral phosphines, leaving intact the icosahedral (or dicapped antiprismatic) structure of the Au_{10} centred cage. In this compound, too, the gold atoms would have an electronic configuration with 16 electrons. Similarly, it could be suggested that the compounds considered as $Au_{12}L_8X_4$, with $L=P(C_2H_5)(C_6H_5)_2$, are instead $Au_{11}L_7X_3$ of type (a), but it is advisable not to speculate too much, since it may be that some of the original formulae will be confirmed by structural analysis.

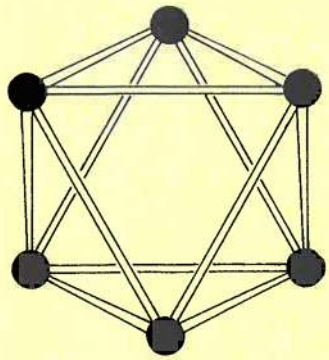

Fig. 6 The $[Au_6L_6]^{2+}$ cluster

As a conclusion, the following provisional generalisations can be made:

(i) The gold clusters obtained so far are neutral compounds or cations containing 6, 9 or 11 gold atoms in which the average oxidation state of the gold varies between 0.33 and 0.2.

(ii) In known structures, one gold atom, not otherwise coordinated, may occupy the centre of the structure; all the other gold atoms are bound to a phosphine or to a nucleophilic anion and to at least four other gold atoms.

(iii) These compounds are electron deficient, since only eight out of the nine gold orbitals are filled.

Only by resolving more structures will we be able to get a deeper insight into this new and interesting class of compound. When more structural information becomes available this may prove useful for the better understanding of the electronic structure of alloys, some of which have atomic patterns similar to those found in these gold clusters.

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Diffusion Barriers for Gold Plated Copper

THE INFLUENCE OF ATOMIC RADIUS

In certain types of circuits the gold plated copper contact elements can operate at moderately high temperatures. In these conditions copper can diffuse through the gold electrodeposit, with the result that any copper reaching the surface will oxidise, thereby increasing the contact resistance and causing further heating, and so increasing the rate of diffusion of copper to the surface. A vicious spiral can be thus created—and complete failure can result.

Nickel is, of course, commonly used as an undercoat for this reason but a research project sponsored by the American Electroplaters' Society to study the usefulness of a range of barrier layers to prevent or minimise this phenomenon has now been the subject of a first report by the two investigators, J. C. Turn of Battelle and Dr E. L. Owen of Kennecott Copper (*Plating*, 1974, **61**, (11), 1015–1018).

Samples of pure copper that had been gold plated without a barrier layer were examined, together with a series of specimens having either an electrodeposited or an electroless deposited metallic barrier between the copper and the electrodeposited gold. The barrier metals were nickel, chromium, platinum, palladium, and rhodium, while electroless deposits of hypophosphite nickel and borane nickel were also employed. There were deposited to thicknesses of 0.25, 0.5, 1.0 and 2.0 μm.

The specimens were diffusion heat treated at 400°C and 550°C in partial vacuum, while those without a barrier layer were also given a 750°C treatment. They were then protected and mounted for microscopic examination to detect any porosity or other defects.

The major part of this investigation involved the use of an electron probe microanalyser. For each specimen a profile of concentration against distance from the interface was determined, and the initial data were adjusted for fluorescence, the effects of atomic number, absorption background, and the finite diameter of the electron beam. Some irregularities were observed in these concentration-distance profiles, and a rather arbitrary factor—"copper penetration"—was therefore established as an alternative indication of the extent of diffusion of the copper into the gold electrodeposit. This was defined as the distance on the corrected copper concentration profile from the original interface to a point corresponding with a concentration of 7.5 weight per cent of copper.

Copper penetration values determined for specimens with barrier layers of platinum, palladium and rhodium at all thicknesses tested showed no significant decreases from the values obtained for specimens without barrier layers, indicating that these metals are ineffective in retarding the penetration of copper.

The pure nickel barriers with a thickness of 1 μm effectively reduced the values of copper penetration as compared with the no-barrier values, while a nickel thickness of 2μm did not generally reduce the copper penetration values below those obtained with the 1μm specimens. This finding does not, of course, agree with the generally accepted idea that increased barrier thickness should increase effectiveness.

Chromium barrier layers in all thicknesses were found to give good results, but chromium has, of course, the associated complication of needing an outgassing treatment to prevent hydrogen blistering, and a special activation step to ensure an adherent gold deposit.

Both the electroless nickel deposits were effective in decreasing copper penetration, the presence of phosphorus in the barrier layer apparently being significantly more effective; an increase in phosphorus content decreased the copper penetration, presumably due to the high volume percentage of nickel phosphide.

Perhaps the most interesting correlation to emerge from these investigations is that between the atomic radius of the barrier layer metal atoms and the degree of copper penetration. The poorer barriers—platinum, palladium and rhodium—all have atomic radii larger than that of copper, whereas the effective barriers, nickel and chromium, have a smaller radius than copper. From this relationship the authors suggest that cobalt, with atomic radius 1.252 Å compared with copper at 1.276 Å, should be examined for its effectiveness as a means of retarding diffusion into gold electrodeposits.

L. B. H.